

Compounds with Intermediate Spin.

I. The Crystal Structure of Tris(*N,N*-dimethyldithiocarbamato)iron(III) at 150 and 295 K

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$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$ has a temperature-dependent magnetic moment. Its crystal structure has been determined from X-ray intensities collected with a four-circle single-crystal diffractometer at 150 ($\mu_{\text{eff}} = 2.4$ BM) and 295 K (4.1 BM). The space group is *Pbca* with $Z = 8$ at both temperatures: $a = 17.419(5)$, $b = 20.272(5)$, $c = 10.060(2)$ Å at 150 K; $a = 17.569(2)$, $b = 20.518(2)$, $c = 10.118(1)$ Å at 295 K. The refinements converged to $R = 0.058$ and 0.067 at 150 and 295 K respectively. At both temperatures mononuclear tris(*N,N*-dimethyldithiocarbamato)iron(III) complexes of pseudosymmetry D_3 are kept together by van der Waals forces. The main structural difference between 150 and 295 K lies in the Fe–S distances: the average length is $2.339(3)$ Å at 150 K and $2.395(5)$ Å at 295 K.

Introduction

Magnetic-susceptibility measurements show that the effective magnetic moment μ_{eff} of a number of tris(*N,N*-diorganodithiocarbamato)iron(III) complexes is strongly dependent on temperature (White, Roper, Kokot, Waterman & Martin, 1964; Ewald, Martin, Ross & White, 1964; Ewald, Martin, Sinn & White, 1969). An example is depicted in Fig. 1. The value of μ_{eff} for tris(*N,N*-dimethyldithiocarbamato)iron(III) increases continuously from 2.08 BM (Bohr magnetons) at 80 K to 4.87 BM at 420 K (Nygren, 1976). The compound decomposes at higher temperatures. The spin-only high-spin value of Fe^{III} (a d^5 ion) is 5.92 BM, while a normal range of its low-spin values in cubic symmetry is 2.0–2.3 BM (Griffith, 1961; Figgis, 1961*a,b*).

In order to describe the temperature dependence of μ_{eff} in the Fe^{III} dithiocarbamates and related compounds, the so-called cross-over model has often been

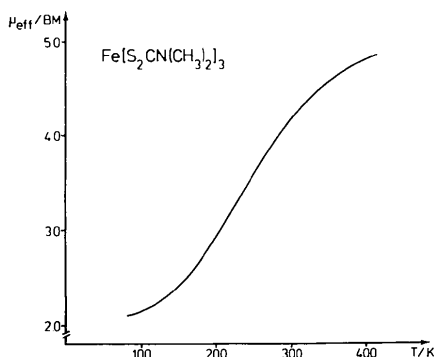
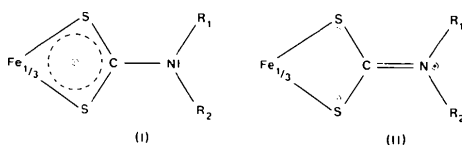


Fig. 1. The effective magnetic moment of tris(*N,N*-dimethyldithiocarbamato)iron(III) as a function of temperature. The measurements were made with the Faraday method (Nygren, 1976).

applied (Ewald, Martin, Ross & White, 1964). If the energy difference between the two possible ground terms 6A_1 and 2T_2 of Fe^{III} (assuming O_h symmetry of the FeS_6 core) is of the order of $k_B T$, a change in temperature results in a change in the relative occupancy of the sextet and doublet states and, thus, a change in μ_{eff} (Griffith, 1961). Van Vleck's equation applied with four adjustable parameters to the temperature dependence of μ_{eff} of the dimethyl compound (Fig. 1) results, for example, in a zero-point energy separation of 392 cm^{-1} between 2T_2 and 6A_1 (Ewald, Martin, Sinn & White, 1969). The value of $k_B T$ at 300 K is 208 cm^{-1} . Mössbauer spectra fail, however, to give evidence of a simultaneous population of two electronic levels in the Fe^{III} dithiocarbamates (Merrithew & Rasmussen, 1972; Eley, Duffy & Uhrich, 1972). If a high-spin/low-spin equilibrium does exist in these compounds, as might be indicated by EPR experiments (Flick & Gelerinter, 1973), the cross-over between the electronic levels must have a frequency larger than 10^7 Hz. Merrithew & Rasmussen (1972) have tried to resolve this difficulty by proposing an alternative model based on calculations by Harris (1968*a,b*). If spin-orbit coupling between sextet, quartet, and doublet states is allowed for in tetragonally distorted octahedral complexes of Fe^{III} the spin is no longer a good quantum number. The ground state of Fe^{III} may be a spin-mixed state, the character of which changes with temperature, resulting in a strongly temperature-dependent μ_{eff} . This model quantitatively describes the variation in μ_{eff} for a series of Fe^{III} haemoglobin derivatives. Magnetic measurements by Butcher & Sinn (1976*a,b*) suggest that the dichloromethane and chloroform solvates of tris(4-morpholinecarbodithiatio-*S,S'*)iron(III) have a quartet ground state and that it is likely that besides doublet

and sextet states quartet states are also low-lying in many Fe^{III} dithiocarbamate complexes. It might thus be possible to obtain results similar to those of Harris (1968*a,b*) for the Fe^{III} dithiocarbamates also.

It has been suggested that the Fe—S bonding in the Fe^{III} dithiocarbamates may be described by the limiting structures (I) and (II) (Eley, Myers & Duffy, 1972; Gregson & Doddrell, 1975). In (I), partially filled Fe^{III} *d* orbitals interact with empty ligand π orbitals arising from the S *d* orbitals. This back-donation is diminished in (II) as the S now accepts electron density from the N atom. The relative importance of (I) and (II) should depend upon the inductive strength of the substituents *R* and on steric interferences caused by them, inhibiting the necessary planar configuration of the S₂CNC₂ group in (II).



The present series of investigations aims at correlating the temperature-dependent magnetic behaviour of some solid Fe^{III} dithiocarbamates with their geometrical features: (i) bond distances and angles in the FeS₆ core and S₂CNC₂ group, (ii) the symmetry of the FeS₆ core and (iii) the planarity of the S₂CNC₂ group, *i.e.* possible evidence of steric interference of the R₁R₂N residues. The crystal structures are determined both at a low

temperature (a low value of μ_{eff} , in most cases) and at room temperature (an intermediate or high value of μ_{eff}). Only one previous study of this type of compound has been made at two different temperatures. Leipoldt & Coppens (1973) measured tris(*N,N*-diethyldithiocarbamato)iron(III) at 79 K ($\mu_{\text{eff}} = 2.2$ BM) and at 297 K (4.3 BM). In this paper we report the crystal structure of tris(*N,N*-dimethyldithiocarbamato)iron(III) at 150 K (2.4 BM) and 295 K (4.2 BM) and the variation of its unit-cell dimensions in the temperature interval 125–295 K.

Experimental

Fe[S₂CN(CH₃)₂]₃ was prepared in a nitrogen atmosphere. A solution of Fe^{III} chloride in ethanol was slowly added to an ethanol solution of equal amounts of sodium hydroxide, carbon disulphide, and dimethylamine. The precipitate was dissolved in chloroform. Black single crystals (tabular **a**) were grown from this solution by slowly adding ethanol. The crystals were insensitive to air. The composition of the compound was checked by elemental analyses of C, H, N and Fe.

Table 1 gives information concerning the crystal data, the collection and reduction of the intensity data sets, and the refinements based on them. Weissenberg photographs show that Fe[S₂CN(CH₃)₂]₃ crystallizes in the Laue class *mmm* with the reflexions *Ok*l: *k* ≠ 2*n*, *h*0*l*: *l* ≠ 2*n*, *hk*0: *h* ≠ 2*n* absent. No change of space group is detected on cooling. A four-circle single-

Table 1. *Crystal data, collection and reduction of intensities, and the least-squares refinement*

Unit-cell dimensions are given in Table 2.			
Temperature (K)	150		295
FW		416.4	
Crystal system		Orthorhombic	
Space group		<i>Pbca</i>	
<i>Z</i>		8	
<i>D_x</i> (g cm ⁻³)	1.55		1.52
Crystal size (mm)		0.15 × 0.20 × 0.25	
Radiation (graphite monochromated)	Mo <i>K</i> α		Cu <i>K</i> α
Take-off angle (°)	3		5
ω -interval (°) (ω -2 θ scan)	0.9 + 1.0 tan θ		0.7 + 0.5 tan θ
θ -interval (°)	3–25		5–70
Minimum number of counts in a scan		3000	
Maximum recording time (s)		180	
μ (cm ⁻¹)	14.3		128.4
Range of the transmission factor	0.746–0.852		0.119–0.423
Number of measured reflexions	3087		3432
Number of reflexions given zero weight [<i>I</i> < 2 σ_c (<i>I</i>)]	791		953
Number of independent reflexions used in the final refinements, <i>m</i>	2296		2485
Number of parameters refined, <i>n</i>		173	
$R = \sum F_o - F_c / \sum F_o $	0.058		0.067
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.069		0.079
$S = \{\sum w(F_o - F_c)^2 / (m - n)\}^{1/2}$	1.9		1.6
<i>C</i> (weighting function)	3.8 × 10 ⁻⁴		1.0 × 10 ⁻³

Table 2. *The unit-cell dimensions of Fe[S₂CN(CH₃)₂]₃ in the interval 125–295 K*

Numbers in parentheses represent estimated standard deviations in the last significant digits.

<i>T</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>
125 K	17.380 (6) Å	20.252 (5) Å	10.051 (2) Å	3537 (2) Å ³
150	17.419 (5)	20.272 (5)	10.060 (2)	3552 (2)
175	17.438 (5)	20.309 (4)	10.070 (1)	3566 (1)
200	17.467 (5)	20.348 (4)	10.082 (1)	3583 (1)
225	17.510 (5)	20.404 (4)	10.096 (2)	3607 (1)
250	17.535 (3)	20.449 (3)	10.103 (1)	3623 (1)
295	17.569 (2)	20.518 (2)	10.118 (1)	3647 (1)

crystal diffractometer (CAD-4) was used in the data collection. Unit-cell dimensions at seven temperatures in the interval 125–295 K were obtained from the θ values of 45 reflexions (Cu $K\alpha_1$ radiation, $\lambda = 1.540562$ Å). The method is described by Danielsson, Grenthe & Oskarsson (1976) together with the low-temperature apparatus. The unit-cell dimensions are given in Table 2.

During the data collection three standard reflexions were checked after every 100 measurements. No systematic variation in their intensities was observed. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization, and absorption effects [$\sigma_c(I)$ is based on counting statistics]. The expression used in the polarization correction was $p = (\cos^2 2\theta_M + \cos^2 2\theta)/(1 + \cos^2 2\theta_M)$ where θ_M is 6.08° for Mo $K\alpha$ and 13.28° for Cu $K\alpha$ radiation.

Structure determination and refinement

The position of Fe³⁺ was deduced from a vector map. A subsequent difference synthesis revealed all the non-hydrogen atoms.

The parameters were refined by full-matrix least squares. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights calculated from $w^{-1} = \sigma_c^2(|F_o|^2)/4|F_o|^2 + C|F_o|^2$. C was adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ in different $|F_o|$ and $\sin\theta$ intervals were obtained. Two scale factors, the positional parameters, and anisotropic thermal parameters were refined at both temperatures (Table 1).

A final difference synthesis was featureless for the 295 K data. The 150 K data gave weak indications of the positions of the methyl H atoms. As attempts to refine these positions were unsuccessful H atoms were excluded.

The scattering factors were taken from *International Tables for X-ray Crystallography* (1968). No correction for anomalous dispersion was included. Table 3 gives the final positional parameters.*

Description of the structure

The compound has almost the same structure at high and low temperature. The building block is the mono-

* Lists of structure factors and thermal parameters together with the root-mean-square components of thermal displacement along the ellipsoid axes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32355 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Positional parameters ($\times 10^5$) of the non-H atoms of Fe[S₂CN(CH₃)₂]₃, with estimated standard deviations*

	150 K			295 K			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	
Fe	56345 (6)	12218 (5)	34108 (9)	Fe	56373 (5)	12190 (5)	33777 (10)
S(1)	47174 (11)	8023 (9)	19455 (18)	S(1)	46928 (10)	8149 (10)	18857 (19)
S(2)	48255 (12)	21143 (10)	29310 (20)	S(2)	48210 (11)	21248 (9)	28628 (22)
N(1)	37693 (38)	17529 (38)	11155 (66)	N(1)	37668 (34)	17570 (40)	10846 (74)
C(1)	43542 (40)	15842 (36)	18788 (69)	C(1)	43424 (36)	15897 (37)	18380 (69)
C(2)	33799 (49)	12723 (50)	2479 (84)	C(2)	33902 (52)	12761 (56)	2112 (96)
C(3)	34751 (55)	24509 (50)	11378 (99)	C(3)	34834 (50)	24488 (54)	10851 (113)
S(3)	64128 (11)	2879 (9)	31482 (18)	S(3)	64224 (10)	2765 (9)	30588 (18)
S(4)	65696 (11)	15300 (9)	18527 (17)	S(4)	66057 (10)	15263 (8)	18075 (17)
N(2)	75966 (33)	5584 (30)	15219 (54)	N(2)	76013 (31)	5590 (27)	14768 (55)
C(4)	69569 (39)	7643 (32)	20864 (61)	C(4)	69579 (34)	7564 (30)	20366 (58)
C(5)	79132 (46)	-1044 (35)	17806 (79)	C(5)	78977 (43)	-1049 (36)	17339 (84)
C(6)	80382 (44)	9904 (35)	6317 (71)	C(6)	80495 (38)	9882 (37)	5921 (74)
S(5)	63060 (10)	17466 (9)	51055 (17)	S(5)	63077 (9)	17491 (9)	51140 (17)
S(6)	50661 (11)	8497 (9)	53802 (17)	S(6)	50761 (9)	8454 (9)	53944 (17)
N(3)	58074 (37)	13686 (26)	74914 (57)	N(3)	58090 (34)	13608 (25)	74594 (55)
C(7)	57282 (38)	13340 (29)	61838 (61)	C(7)	57421 (33)	13299 (28)	61744 (63)
C(8)	52717 (52)	10294 (42)	84094 (76)	C(8)	52887 (55)	10215 (43)	83691 (81)
C(9)	64243 (47)	17564 (38)	81041 (72)	C(9)	64174 (47)	17509 (40)	80682 (75)

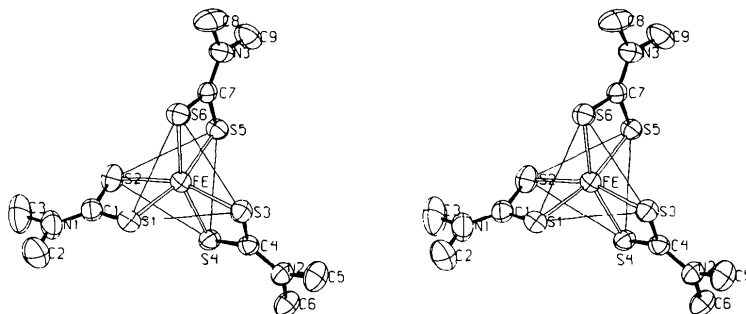


Fig. 2. A stereoscopic pair of drawings of tris(*N,N*-dimethyldithiocarbamato)iron(III). The thermal ellipsoids are scaled to include 50% probability.

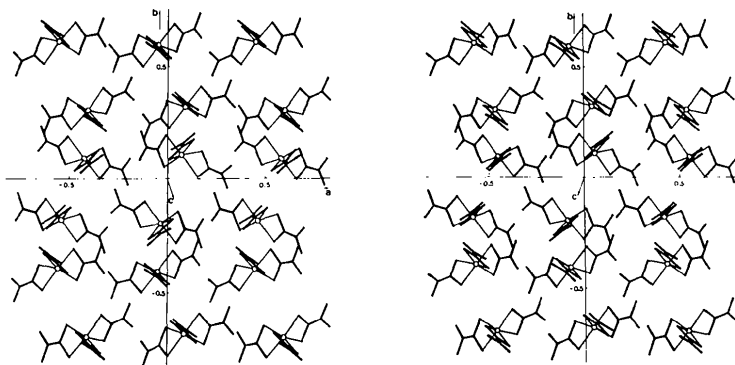


Fig. 3. The crystal packing of $\text{Fe}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$. Space group *Pbc*₁.

Table 4. Selected interatomic distances (Å) and angles (°) with estimated standard deviations

	150 K	295 K		150 K	295 K
(a) The FeS_6 polyhedron					
Fe—S(1)	2.334 (2)	2.392 (2)	S(1)—S(3)	3.358 (3)	3.444 (3)
Fe—S(2)	2.344 (2)	2.405 (2)	S(1)—S(6)	3.510 (3)	3.614 (3)
Fe—S(3)	2.344 (2)	2.397 (2)	S(3)—S(6)	3.441 (3)	3.541 (2)
Fe—S(4)	2.345 (2)	2.412 (2)	S(2)—S(4)	3.436 (3)	3.533 (3)
Fe—S(5)	2.325 (2)	2.378 (2)	S(2)—S(5)	3.463 (3)	3.550 (3)
Fe—S(6)	2.340 (2)	2.392 (2)	S(4)—S(5)	3.334 (2)	3.417 (2)
S(1)—S(2)	2.845 (3)	2.873 (3)	S(1)—S(4)	3.549 (3)	3.665 (3)
S(3)—S(4)	2.848 (3)	2.878 (2)	S(3)—S(5)	3.558 (3)	3.673 (3)
S(5)—S(6)	2.837 (3)	2.864 (2)	S(6)—S(2)	3.581 (3)	3.695 (3)
(b) Ligand 1					
S(1)—C(1)	1.708 (7)	1.706 (8)	S(1)—C(1)—S(2)	112.3 (4)	113.5 (4)
S(2)—C(1)	1.718 (7)	1.728 (7)	S(1)—C(1)—N(1)	123.6 (6)	122.6 (6)
C(1)—N(1)	1.321 (10)	1.312 (9)	S(2)—C(1)—N(1)	124.4 (6)	123.9 (6)
N(1)—C(2)	1.474 (11)	1.481 (13)	C(1)—N(1)—C(2)	121.9 (7)	121.1 (8)
N(1)—C(3)	1.504 (12)	1.504 (13)	C(1)—N(1)—C(3)	119.8 (7)	120.1 (7)
			C(2)—N(1)—C(3)	118.3 (7)	118.8 (7)
			C(5)—N(2)—C(6)	117.0 (6)	117.8 (6)
(c) Ligand 2					
S(3)—C(4)	1.724 (7)	1.710 (6)	S(3)—C(4)—S(4)	112.2 (4)	114.5 (3)
S(4)—C(4)	1.708 (7)	1.712 (6)	S(3)—C(4)—N(2)	123.6 (5)	123.4 (5)
C(4)—N(2)	1.319 (9)	1.328 (8)	S(4)—C(4)—N(2)	124.2 (5)	122.1 (5)
N(2)—C(5)	1.476 (9)	1.481 (9)	C(4)—N(2)—C(5)	121.9 (6)	120.3 (6)
N(2)—C(6)	1.470 (9)	1.482 (9)	C(4)—N(2)—C(6)	121.6 (6)	121.9 (6)
(d) Ligand 3					
S(5)—C(7)	1.699 (6)	1.697 (6)	S(5)—C(7)—S(6)	112.3 (4)	113.6 (4)
S(6)—C(7)	1.717 (7)	1.726 (6)	S(5)—C(7)—N(3)	123.1 (5)	123.5 (5)
C(7)—N(3)	1.325 (8)	1.307 (8)	S(6)—C(7)—N(3)	124.6 (5)	122.9 (5)
N(3)—C(8)	1.482 (10)	1.472 (11)	C(7)—N(3)—C(8)	121.9 (6)	122.9 (6)
N(3)—C(9)	1.467 (10)	1.471 (10)	C(7)—N(3)—C(9)	121.5 (6)	120.6 (6)
			C(8)—N(3)—C(9)	116.6 (6)	116.5 (6)

nuclear tris(*N,N*-dimethyldithiocarbamato)iron(III) complex shown in Fig. 2. The only packing force between the complexes is of van der Waals type. Fig. 3 shows the packing arrangement in the crystal. The closest contacts between the complexes are across the symmetry centre with Fe–Fe = 6.29 at 150 K and 6.39 Å at 295 K. Table 4 gives selected interatomic distances and angles.

The coordination polyhedron

Six S atoms form a twisted trigonal prism of approximately D_3 symmetry around the Fe atom. The true symmetry is C_1 . The mean Fe–S bond length is 2.339 (3) Å at 150 K and 2.395 (5) Å at 295 K. Table 5 gives some characteristics of the geometry of the coordination polyhedron compared with the geometry of an O_h octahedron and a D_3 trigonal prism. The two triangular faces are only approximately equilateral. The average edge length increases 0.1 Å between 150 and 295 K. The height of the prism, measured as the distance between the centroids of the triangular faces, is almost the same at the two temperatures but 12% less than required for a true octahedron. The ligands constrain the triangular faces of the prism to be rotated

Table 5. *The geometry of the coordination polyhedron*

	150 K	295 K	O_h	D_3
Edge of triangular face	3.42 Å	3.52 Å	a	a
Height of prism	2.50 Å (0.72 a)	2.53 Å (0.71 a)	0.816 a	–
Torsion angle	40°	38°	60°	–
Tilt angle (between the triangular faces)	1.8°	1.9°	0	0
Fe ³⁺ –centre of prism	0.033 Å	0.039 Å	0	0
Ligand bite	2.84 Å (0.83 a)	2.87 Å (0.82 a)	a	–

Table 6. *Deviations ($\text{Å} \times 10^3$) from the least-squares planes through the S_2CN groups*

150 K					
S(1)	–2	S(3)	0	S(5)	4
S(2)	–2	S(4)	0	S(6)	4
N(1)	–2	N(2)	0	N(3)	6
C(1)	6	C(4)	0	C(7)	–14
C(2)	–16	C(5)	–28	C(8)	–76
C(3)	–23	C(6)	–10	C(9)	90
Fe	130	Fe	–148	Fe	86
295 K					
S(1)	–1	S(3)	–2	S(5)	2
S(2)	–1	S(4)	–2	S(6)	2
N(1)	–1	N(2)	–3	N(3)	3
C(1)	2	C(4)	6	C(7)	–6
C(2)	–22	C(5)	–37	C(8)	–76
C(3)	1	C(6)	9	C(9)	79
Fe	–110	Fe	–165	Fe	89

relative to one another. The resulting torsion angles are calculated by method 1 of Dymock & Palenik (1975).

The ligands

The interatomic distances and angles in the *N,N*-dimethyldithiocarbamate ligands (Table 4) are similar to those found, for example, in $Tl[S_2CN(CH_3)_2]$ (Jennische & Hesse, 1973) and $Cu[S_2CN(CH_3)_2]_2$ (Einstein & Field, 1974) and in the relevant parts of $Fe[S_2CN(C_2H_5)_2]_3$ (Leipoldt & Coppens, 1973). Table 6 gives the deviations of the non-H ligand atoms from the least-squares plane through the S_2CN group. The maximum deviation of a methyl C atom from this plane is 0.09 Å, in ligand 3 at 150 K. All the bonds in the S_2CN groups have partial double-bond character.

Is there a significant difference between the ligand geometries at 150 and 295 K? To answer this question we have used probability-plot analysis to compare the ligand bond distances and angles at the two temperatures. Ordered values of $\delta d_i = |d(150)_i - d(295)_i| / [\sigma^2 d(150)_i + \sigma^2 d(295)_i]^{1/2}$ are compared in Fig. 4 with the values expected for a half-normal distribution of zero mean and unit variance (DeCamp, 1973; Albertsson & Schultheiss, 1974). Torsion angles are excluded by only using interatomic distances $d(T)$, less than 2.90 Å in the comparison. All except three points, representing the three ligand bites (S–S) in the complex, are compatible with a straight line with zero intercept and slope 1.51. The interatomic distances are uncorrected for the decrease in the thermal parameters between 295 and 150 K, as the molecules do not behave as rigid bodies. This can be seen by comparing the directions of the thermal ellipsoid axes in Fig. 2. That a straight line with zero intercept is obtained in Fig. 4 indicates that the systematic error possibly introduced by not correcting for thermal motion should be very small. Disregarding it, we might conclude that on average the standard deviations in the two structure determinations are underestimated by the factor 1.5 and that the ligand bond distances and angles, except S–C–S, are the same at both temperatures. The S–S

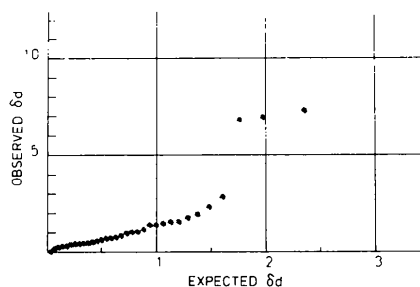


Fig. 4. A half-normal probability-plot comparison of interatomic distances less than 2.90 Å in $Fe[S_2CN(CH_3)_2]_3$ at 150 and 295 K. The slope is 1.51 and the intercept 0.01.

ligand bite distances are, on average, increased from 2.843 (3) Å at 150 K to 2.872 (4) Å at 295 K (Table 4).

Discussion

The structures of four Fe^{III} dithiocarbamates have been determined at room temperature, besides the present study and the study at 79 and 297 K of tris(*N,N*-diethyldithiocarbamato)iron(III) by Leipoldt & Coppens (1973); tris(*N,N*-di-*n*-butyldithiocarbamato)iron(III) ($\mu_{\text{eff}} = 5.3$ BM) by Hoskins & Kelly (1968); tris(*N*-methyl-*N*-phenyldithiocarbamato)iron(III) (2.9 BM) by Healy & White (1972); tris(4-morpholinocarbodithiato-*S,S'*)iron(III) (5.1 BM) by Healy & Sinn (1975) (dichloromethane solvate) and by Butcher & Sinn (1976*b*) (chloroform and water solvates); and tris(1-pyrrolidinocarbodithiato-*S,S'*)iron(III) (5.9 BM) by Sinn (1976) (benzene solvate) and by Healy & White (1972).

All the complexes so far studied have the pseudo-symmetry D_3 . The torsion angle of the trigonal FeS₆ prisms lies in the interval 33–41° with slightly larger angles in the low- than in the high-spin complexes. The only significant changes detected in the complex geometries when μ_{eff} changes occur in the FeS₆ core: the Fe–S length increases from a low-spin value of about 2.32 to a high-spin value of about 2.43 Å. This difference is compatible with the difference, 0.10 Å, between the high- and low-spin radii of Fe³⁺ (Shannon, 1976).

The average increase in the Fe–S bond length in tris(*N,N*-dimethyldithiocarbamato)iron(III) is 0.058 (2) Å when μ_{eff} increases from 2.4 to 4.2 BM. Crystal packing makes the change in unit-cell volume V with temperature less than could be expected from the change in the Fe–S lengths. Using the data in Table 2 and Fig. 1 we have plotted V vs μ_{eff} in Fig. 5. The points fall on a smooth curve. From its shape we conclude that there is

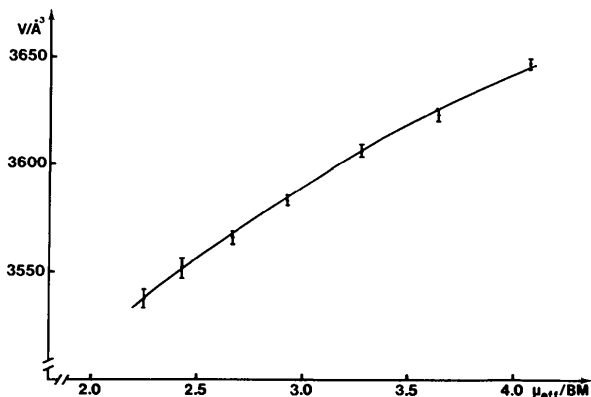


Fig. 5. Unit-cell volume as a function of the effective magnetic moment in the interval 125–295 K.

a continuous increase in the size of the FeS₆ core and, consequently, of the complex when μ_{eff} increases.

If the intermediate spin state $\mu_{\text{eff}} = 4.2$ BM is a result of a simultaneous occupation of a high- and a low-spin electronic level, the corresponding time-averaged crystal structure observed in the diffraction experiment at 295 K would be a superposition of two molecular geometries of the Fe^{III} complex. One geometry should correspond to the low-spin radius of Fe³⁺ and the other to the high-spin radius. Leipoldt & Coppens (1973) have, however, shown that the apparent increase in thermal parameters caused by this disorder, is too small to be detected in a room-temperature analysis.

The S–C and C–N bonds have a partial double-bond character at both low and high values of μ_{eff} in all the investigated Fe^{III} dithiocarbamates. As shown by limiting structures (I) and (II), this indicates some degree of Fe–S π -bonding irrespective of the spin-state of Fe^{III}. The ¹³C NMR study by Gregson & Doddrell (1975) indicates that the metal–ligand π -bonding increases when μ_{eff} decreases. Within the present limit of errors this result cannot be confirmed by the bond distances in the various S₂CNC₂ groups as they appear to be unaffected by a changed spin state of Fe^{III}. All the investigated complexes also appear to have S₂CNC₂ groups as planar as in the present complex.

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The Crystal Structure of Cyanato(2-dimethylaminoethanolato)copper(II), $C_5H_{10}N_2O_2Cu$

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The title compound is monoclinic, space group $P2_1/c$, with $a = 18.57(2)$, $b = 17.29(2)$, $c = 19.87(2)$ Å, $\beta = 98.2(1)^\circ$, $Z = 32$. The structure has been refined to a final R of 0.091 for 4138 independent counter reflexions. Two crystallographically different but very similar cubane-like tetramers are built up from two dimers. The mean values for the intramolecular Cu–Cu separations are 2.92 (inside a dimer) and 3.44 Å (between two dimers). The Cu coordination is approximately square pyramidal with Cu bonded to two O atoms (inside the dimer, mean Cu–O 1.96 Å), the amino N atom (mean Cu–N 2.05 Å), and the N of the cyanato group (mean Cu–N 1.88 Å). The apical position of the pyramid is occupied by one O atom of the second dimer (mean Cu–O 2.48 Å).

Introduction

Different types of structures in the solid state have been found to be built up by thiocyanato(2-dialkylaminoethanolato)copper(II) complexes. Polymeric structures have been reported for the complexes containing *N,N*-dimethylamino (Haase, Mergehenn & Krell, 1976) and *N,N*-diethylamino (Pajunen & Smolander, 1974) groups; a tetrameric cubane-like structure is realized by thiocyanato(2-dibutylaminoethanolato)copper(II) (Mergehenn & Haase, 1977b). These structural properties are analogous to those of the halogeno complexes (e.g. Matsumoto, Ueda, Nishida & Kida, 1976; Mergehenn, Haase & Allmann, 1975). Here we present the first structural investigation of complexes of the cyanato series, which are found to be tetrameric in most cases (Merz & Haase, 1977; Mergehenn & Haase, 1977b), but with different molecular properties.

Experimental

The preparation of cyanato(2-dimethylaminoethanolato)copper(II) followed closely that reported by Lehtonen, Luukkonen & Uggla (1971). Instead of KSCN an equivalent amount of KOCN was used and the precipitate recrystallized from methanol.

A needle-like crystal with the following dimensions was used for the structure determination: $\{100\} - \{100\} = \{010\} - \{0\bar{1}0\} = 0.15$, $\{001\} - \{00\bar{1}\} = 0.87$ mm (distances from face to face). The measurements were carried out on a computer-controlled Stoe four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation.

Cell dimensions and the orientation matrix were obtained by a least-squares fit of 20 strong reflexions to the setting angles. For the intensity collection the $\omega/2\theta$ scan technique was used ($3^\circ \leq 2\theta \leq 42^\circ$); the measuring time for the reflexions (60 s) was twice the time for